

We thank the anonymous reviewers for taking the time to carefully review our original paper. Below we address their comments in turn (see Pages 8 and 16 of this response), but first we wish to note one significant change made to the model setup and results in response to the reviewer's comments.

Both reviewers noted that an overestimate of the initial concentrations of the SVOC species could account for the overestimate of OA seen when the Grieshop et al. (2009a), Robinson et al. (2007), and Ahmadov et al. (2012) chemical mechanisms are used. Based on this, we revisited our calculations of the initial concentrations of the SVOC species and did uncover a significant error. We apologize for the error, and thank the reviewers for drawing our attention to it. While this does not change our qualitative conclusions, it does affect the quantitative results for OA significantly, and so before we address the specific comments we wish to describe our revised approach and the changes that we have made to the revised paper as a result.

Initial SVOC concentrations

We have added a new Table (Table 1 in the revised paper, reproduced below for convenience) that includes additional information on the SVOC species, including their saturation mass concentrations, their molecular weights, and the POA total mass fractions used in Grieshop et al. (2009a) and in this study.

The key difference in the POA mass fractions is that Grieshop et al. (2009a) were only able to measure species with a saturation mass concentration (C^*) of $10^4 \mu\text{g m}^{-3}$ or less. At the measured temperature (288.4 K) and initial concentration of organic aerosol in the Williams fire smoke plume ($849 \mu\text{g m}^{-3}$), the Grieshop et al. (2009a) POA distribution implies that 81% of the total mass of SVOC species SVOC₁ to SVOC₇ is in the aerosol phase, leaving $200 \mu\text{g m}^{-3}$ of SVOC species in the gas phase.

However, Akagi et al. (2011) provide an emission factor for unidentified non-methane organic compounds (NMOCs) from Savannah/Grassland fires, which we can use to calculate an emission ratio of 0.195 g unidentified NMOC/g CO (with an uncertainty of ~50%).¹ Since we have an initial CO concentration of 10,000 ppb of CO ($=10,276 \mu\text{g/m}^3$ CO at 288.4K and 880 hPa), we get an estimate of about $2000 \mu\text{g/m}^3$ of unidentified NMOCs in the gas-phase of the smoke. So to be consistent with the EFs of Akagi et al. (2011), there still needs to be another $\sim 1800 \mu\text{g/m}^3$ of unidentified NMOCs initially in the plume with $C^* > 10^4 \mu\text{g/m}^3$. These remaining unidentified NMOCs can be included in ASP v2.1 as either SVOC₈ ($C^* = 10^5 \mu\text{g/m}^3$) or SVOC₉ ($C^* = 10^6 \mu\text{g/m}^3$). In Table 1 we chose to consider all of the remaining unidentified NMOCs as SVOC₈ in

¹ Note that the unidentified NMOC/CO ratio for Chaparral in Akagi et al. (2011) (revised in Yokelson et al., 2013) is approximately 50% lower than the Savannah value used here, but this lower value is within the 50% uncertainty range we test in our sensitivity studies, described below and in the revised paper. As noted in the revised paper (P17, L15-19), we used the Savannah value from Akagi et al. (2011) as both ratios were estimated a twice the total to the identified NMOCs, and thus the difference in the estimates are mainly due to the fact that fewer NMOC species had been identified for chaparral fires.

our updated model runs, but we have performed sensitivity tests where they are considered as SVOC₉ instead.

Table 1. Definition of SVOC species following Grieshop et al. (2009a).

Species	C^* ($\mu\text{g m}^{-3}$ @ 300 K)	ΔH_{vap} (kJ mol^{-1})	MW (g mol^{-1})	POA volatility distributions ^a	
				Grieshop et al. (2009a)	This study ^b
SVOC ₁	10^{-2}	77	524	0	0
SVOC ₂	10^{-1}	73	479	0	0
SVOC ₃	10^0	69	434	0.1	0.038
SVOC ₄	10^1	65	389	0.14	0.0532
SVOC ₅	10^2	61	344	0.33	0.1254
SVOC ₆	10^3	57	299	0.33	0.1254
SVOC ₇	10^4	54	254	0.1	0.038
SVOC ₈	10^5	50	208	0	0.62
SVOC ₉	10^6	46	163	0	0

^aRelative mass emissions in each volatility bin.

^bWhere the relative amounts of SVOC_{*i*} (*i*=1 to 7) are kept as in Grieshop et al. (2009a), but additional organic mass is added to SVOC₈ to account for the unidentified NMOC mass reported by Akagi et al. (2011).

Our revised estimate of the total gas-phase SVOC concentrations are significantly smaller (by a factor of about 2.5) than the erroneous values used in our original paper. The major impact of this correction is on the OA results shown in Figure 9. The revised Figure 9 is shown below for convenience. Note that the scale of this figure has changed from the original paper because now the Grieshop et al. (2009a) chemical mechanism only overestimates OA by a factor of 3.7 instead of 7.2 as in the original paper. Generally the mechanisms with $k_{OH} \geq 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (e.g., Grieshop et al., 2009a and Robinson et al., 2007) show a roughly proportional change in predicted OA concentrations downwind when the smaller SVOC concentrations are used, while the mechanisms with $k_{OH} = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ show smaller impacts, as the decrease in SVOC volatility due to reaction with OH is less rapid in these cases, and so they are less sensitive to the amount of mass initially in the more-volatile SVOC₈ and SVOC₉ bins. However, the qualitative conclusions of the analysis stay similar – the Grieshop et al. (2009a) and Robinson et al. (2007) mechanisms give too much OA, and adding half-fragmentation to the Ahmadov et al. (2012) chemical mechanism improves the match with OA *and is consistent with the acetic acid production*. However, in the revised Figure 9 the result for the original Ahmadov et al. (2012) mechanism is also within the error bars of the observed value, and thus we can only say the results are consistent with SVOC fragmentation, not that SVOC fragmentation is required to simulate OA formation in the Williams fire plume.

In addition, the revised initial SVOC concentrations still result in an underestimate of the formation of O_3 and the loss of C_2H_4 and NO_x when the the Grieshop et al. (2009a), Robinson et al. (2007), and Ahmadov et al. (2012) chemical mechanisms are used, as in the original paper. While the gas-phase results change slightly (as discussed in the revised text and in slight changes to Figures 10-14), the parameters for the optimized SVOC chemistry remain the same as in the original paper, as there is still a large amount of SVOC mass present in the gas-phase in the revised model simulations. The major change to the gas-phase results from our original paper is that the PAN overestimate is increased (possibly due to an overestimate of acetaldehyde concentrations), but that the C_2H_4 decay (and thus the average OH concentration) is better represented in the model. We have revised the Abstract and Conclusions sections to reflect this change as noted below.

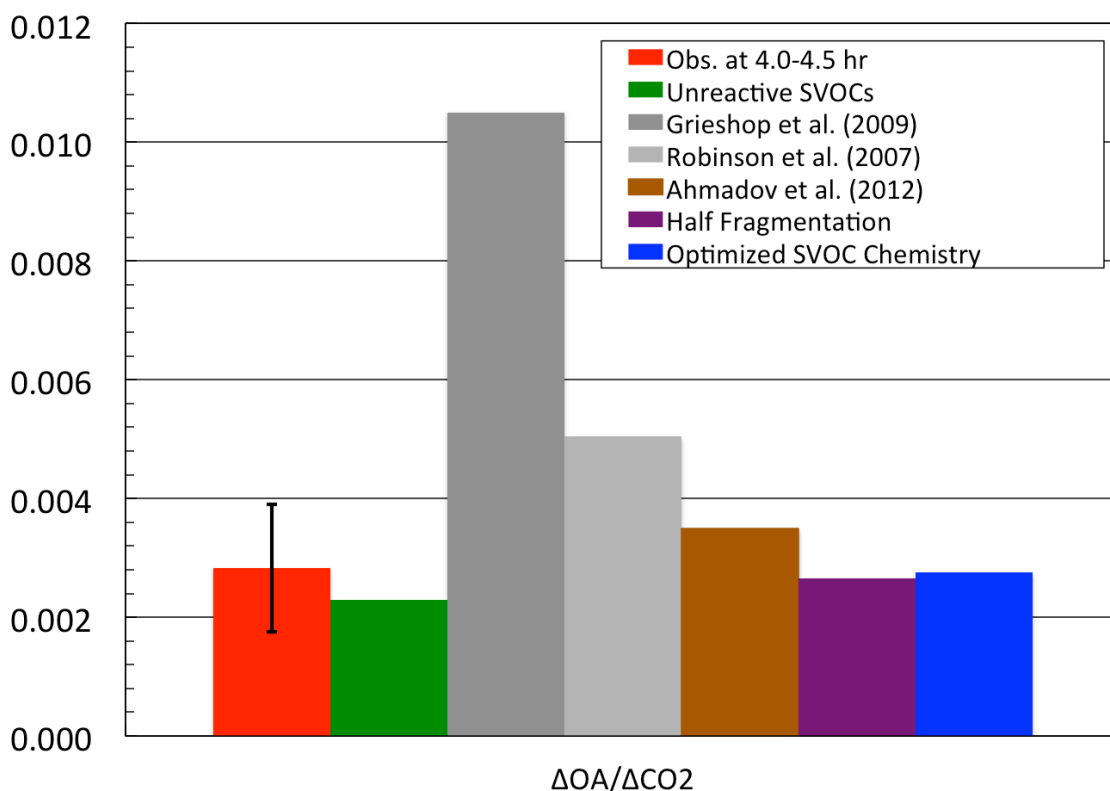


Figure 9. Enhancement ratio (EnR, g/g) of organic aerosol (OA) to CO_2 after 4 to 4.5 hr of smoke aging. The error bars on the observed values are based on the 36% uncertainty in the AMS observations of OA. All model results assume the best-estimate dilution rate and the photolysis rates corresponding to the middle of the plume (solid black line in Figure 5).

Changes to the revised paper due to the new initial SVOC concentrations

Below, new text is shown in italics, and old values are shown struck through where applicable.

P2, L4-6, Abstract:

We show that this method can successfully simulate the observations of O₃, OA, ~~PAN~~, NO_x, C₂H₄, and OH to within measurement uncertainty using reasonable assumptions about the chemistry of the unidentified SVOCs.

P2, L6-8, Abstract:

These assumptions were: (1) a reaction rate constant with OH of $\sim 10^{-11}$ cm³/s; (2) a significant fraction (*up to* $\sim 50\%$) of the RO₂ + NO reaction resulted in fragmentation, rather than functionalization, of the parent SVOC;

P2, L14-15:

However, the model overestimates PAN formation downwind by about 50%, suggesting the need for further refinements to the chemistry.

P17, L1-28: The following language has been added to Section 5.1 to describe the new SVOC initial concentrations:

The volatility distribution for the POA was taken from the wood smoke study of Grieshop et al. (2009a,b). Table 1 shows the POA total mass fractions used for wood smoke in Grieshop et al. (2009a) and the values used in this study for the Williams fire. At the measured temperature (288.4 K) and initial concentration of organic aerosol in the Williams fire smoke plume (849 $\mu\text{g m}^{-3}$), the Grieshop et al. (2009a) POA volatility distribution implies that 81% of the total mass of SVOC species SVOC₁ to SVOC₇ is in the aerosol phase, leaving 200 $\mu\text{g m}^{-3}$ of SVOC species in the gas phase. Note that the May et al. (2013) POA volatility distribution (not shown in Table 1) is more volatile than Grieshop et al. (2009a), with 65% of the total mass of SVOC species SVOC₁ to SVOC₇ in the aerosol phase, leaving about 460 $\mu\text{g m}^{-3}$ of SVOC species in the gas phase.

However, Grieshop et al. (2009a) and May et al. (2013) were only able to measure species with a saturation mass concentration (C) of 10⁴ $\mu\text{g m}^{-3}$ or less. Furthermore, Akagi et al. (2011) provide emission factors for unidentified non-methane organic compounds (NMOCs) from savannah/grassland and chaparral fires, with unidentified NMOCs estimated to be equal in mass to the identified species. The savannah/grassland estimate is about twice as large as the chaparral estimate, as fewer species have been identified in chaparral fires. Here we use the savannah/grassland estimate to calculate an emission ratio of 0.195 g unidentified NMOC/g CO, but assign this value an uncertainty of $\sim 50\%$, consistent with the lower chaparral estimate. This implies that there is about 2000 \pm 1000 $\mu\text{g m}^{-3}$ of unidentified NMOCs in the gas-phase of the smoke. So to be consistent with the EFs of Akagi et al. (2011) and the volatility distributions of Grieshop et al. (2009a) and May et al. (2013), there still needs to be another 1500-1800 $\mu\text{g m}^{-3}$ of unidentified NMOCs initially in the plume with C* $>$ 10⁴ $\mu\text{g m}^{-3}$ which the techniques used by Grieshop et al. (2009) and May et al. (2013) would not have been*

able to measure. These remaining unidentified NMOCs were included as SVOC₈ ($C^* = 10^5 \mu\text{g m}^{-3}$), as shown in Table 1 and Tables S3 and S4 of the Supplemental Material. Below we also discuss sensitivity tests that were performed to see how the results change if the remaining unidentified NMOCs are considered as SVOC₉ ($C^* = 10^6 \mu\text{g m}^{-3}$) instead, as well as for an increase or decrease of the estimated unidentified SVOC concentrations by 50%.

P21, L17-20:

Figure 9 shows the modeled OA enhancement ratios ($\Delta\text{OA}/\Delta\text{CO}_2$, g/g) at 4.5 hours downwind using the parameters listed in Table 2 in addition to the observed average OA enhancement ratio ($2.83 \pm 1.08 \times 10^{-3}$) and the modeled OA enhancement ratio for the case where the chemistry of the unidentified SVOCs is not included (2.27×10^{-3} ~~2.19×10^{-3}~~).

P22, L7-9:

Figure 9 shows that the SVOC mechanisms of Robinson et al. (2007) and Grieshop et al. (2009a,b) overestimated the OA downwind by a factor of 1.8 ~~3.1~~ and 3.7 ~~7.2~~, respectively.

P22, L15-18:

The scheme of Ahmadov et al. (2012), with $k_{\text{OH}} = 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was consistent with the uncertainty in the observations, but slightly higher than the observed value (3.48×10^{-3} versus the observed value of $2.83 \pm 1.08 \times 10^{-3}$). One approach to further reduce the modeled OA would be to reduce k_{OH} even further.

P22, L28-31:

Figure 9 shows that a k_{OH} of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a fragmentation probability of 50% (the “Half Fragmentation” case, see Figure 5) provided a reasonably good match with the observed $\Delta\text{OA}/\Delta\text{CO}_2$ 4.5 hours downwind in the smoke plume (2.63×10^{-3} ~~3.4×10^{-3}~~ versus the observed value of $2.83 \pm 1.02 \times 10^{-3}$).

P23, L30-31 and P24, L1:

Section 5.3 showed that an SVOC mechanism following Reaction R2 with a k_{OH} of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a fragmentation probability α of up to 0.5 (the “Half Fragmentation” scheme in Table 2) could explain the observed evolution of OA in the Williams fire.

P24, L6-10:

For example, Figure 11 shows that using the “Half Fragmentation” scheme reduced the ASP v2.1 estimates of the enhancement ratios of O₃ and PAN downwind by 24% ~~32%~~ and 23% ~~67%~~, respectively (for the best estimate dilution and photolysis case, the black

line in Figure 5), while Figure 12 shows that it increased the ASP v2.1 estimates of C₂H₄ and NO_x downwind by 33% 50% and 151% a factor of 3.3, respectively.

P25, L17-19:

For the *best estimate dilution and photolysis model case (i.e., the solid black line in Figure 5)*, $\Delta\text{OA}/\Delta\text{CO}_2$ is 2.75×10^{-3} ~~3.5×10^{-3}~~ (g/g), very close to the observed value of $2.83 \pm 1.02 \times 10^{-3}$.

P25, L28-31:

For the *best estimate dilution and photolysis model case* $\Delta\text{O}_3/\Delta\text{CO}$ is 0.119 at 4.5 hours downwind, about 25% larger than the observed value of 0.095 ± 0.022 , while the $\Delta\text{PAN}/\Delta\text{CO}_2$ is now 7.56×10^{-4} (~~6.81×10^{-4}~~) at 4.5 hours downwind, about 48% larger than the observed value of $(5.10 \pm 1.21) \times 10^{-4}$.

P26, L3-6:

The NO_x results were much improved from the “half frag” case in Section 5.3, with the *best estimate dilution and photolysis case* $\Delta\text{NO}_x/\Delta\text{CO}_2$ of 1.6×10^{-4} ~~9.6×10^{-5}~~ being below the mean observed value of $4.6 \pm 2.3 \times 10^{-4}$, but consistent with the error bars of the individual samples as shown in Figure 14.

P26, L7-10:

The decay of C₂H₄ is also better modeled than in the Half Fragmentation case, suggesting the model OH is also improved. The modeled OH concentration for the best estimate dilution and photolysis case is now 5.3×10^6 ~~3.2×10^6~~ molecules cm⁻³, matching the observed value of $5.27 \pm 0.97 \times 10^6$ molecules cm⁻³.

P26, L20-22:

For the Williams fire, these assumptions were: (1) a reaction rate constant with OH of $\sim 10^{-11}$ cm³/s; (2) a significant fraction (*up to* $\sim 50\%$) of the RO₂ + NO reaction resulted in fragmentation, rather than functionalization;

P26, L26-28:

However, this chemistry still overestimates PAN formation downwind by about 50%, suggesting the need for further refinements to the chemistry and estimated emission rates of PAN precursors like acetaldehyde.

Fig. 9-14: Figures 9-14 have been updated to reflect the new model results.

Tables S3 and S4 in the supplemental material: The initial concentrations of the SVOC species in the gas and aerosol phases have been updated.

Our responses to the reviewers' specific comments are included below. The reviewer comments are in boldface, while our responses are in plain text with changes to our manuscript shown in italics. Afterward, we discuss other minor edits that were made to our revised manuscript.

Anonymous Referee #1

This paper presents a plume modeling study of a single fire that took place in California in 2009. The study attempts to demonstrate the best fit parameterizations for unidentified VOCs in the fire plume. The paper is rather long (19 figures + tables) and complex. In places, there appears to be some significant missing information and the structure, in my opinion, needs some significant reworking. All of this said, I think the paper contains some important scientific conclusions and given significant editing could be suitable for publication.

The structure and missing information issues are discussed below. Here we discuss the major changes we made to shorten the length of the revised paper.

- Tables 1-4 have been moved to the Supplemental Material, (and a new Table 1 added) so that Table 5 from the original manuscript is now Table 2.
- The description of the EPA chamber in Section 3 has been shortened.
- Section 4, describing the aircraft data for the Williams fire, has been substantially shortened, as most of this information is discussed in detail in Akagi et al. (2012) and the other references in that section.
- Figure 1b, the HCHO comparison for the smog chamber results, has been removed, which also increases the font sizes in Figure 1a (now Figure 1).

But first, scientifically, I think the paper needs a better framing and context. The paper attempts to quantitatively model several gases including O₃, PAN, etc and the OA/CO₂ enhancement ratio in the fire plume using several possible parameterizations of unidentified VOCs. But the observed OA/CO₂ ER actually decreases, presumably due to fragmentation and volatilization of the OA. So in a sense, the authors are attempting to model this decreasing ER, with a process that largely generates increasing ERs, while at the same time not disturbing the gas phase chemistry too much. The authors need to discuss this clearly in the introduction and provide a clear statement of the problem and the goals for this analysis.

The reviewer is correct in their statement of the problem, and we agree that this should be stated more clearly in the introduction. We have made the following changes to the introduction of our revised paper to address this issue (P6, L11-22):

Furthermore, while there was clear secondary formation of O₃ and PAN within the Williams fire plume, the dilution-corrected amount of OA in the plume decreased slightly (Akagi et al., 2012). Most current methods for modeling the OA evolution in smoke plumes lead to significant secondary growth of the OA (e.g., Grieshop et al., 2009a), but we need instead to modify ASP v2.1 to simulate both this slight loss of OA and the chemical formation of O₃, PAN, and other gas-phase species.

Here we present a method for simultaneously accounting for the impact of the unidentified organic compounds (here collectively called “SVOCs”) on the formation of OA and O₃, drawing on the Volatility Basis Set approach (e.g., Robinson et al., 2007) for modeling OA and the concept of the mechanistic reactivity of a mixture of organic compounds (e.g., Carter, 1994). We show that this method can successfully simulate the Williams fire plume observations using reasonable assumptions about the chemistry of the unidentified SVOCs.

One key aspect that is not well explained is the source and meaning of the SVOC concentrations used (Table 4). I looked through the paper but did not find this information, nor is it contained in the caption to table 4[...]

We agree with the reviewer that we did not adequately define the meaning of the SVOC species and the concentrations used. We have added a new Table (Table 1 in the revised paper) that includes additional information on the SVOC species, including their saturation mass concentrations, their molecular weights, and the POA fractions used in Grieshop et al. (2009a) and this study. Tables 3 and 4 from the original paper have been moved to Tables S3 and S4 in the Supplemental Material, and have been updated to reflect the new POA fractions already discussed in Pages 1-7 of this response.

[...]One possible explanation that the authors skip over is that the concentrations of these SVOCs are significantly over-estimated. This needs to be discussed and error bars on the SVOCs should be included.

We agree with the reviewer, and most of our discussion on Pages 1-7 of this response addresses the fact that we found that the SVOCs were indeed overestimated. In order to address this concern, we performed additional sensitivity studies to see how our results could change given the ~50% uncertainty in the mass of the unidentified SVOC compounds present in the gas-phase of the smoke plume.

We ran two sensitivity tests, one where the mass of the unidentified SVOC compounds was increased by 50%, and one where it was decreased by 50%. This uncertainty had a small impact (~ 3%) on the OA formation for our optimized chemistry simulation discussed in Section 5.5, mainly because the unidentified SVOCs are initially placed in a relatively high-volatility bin (SVOC₈) and our optimized chemistry does not rapidly decrease the volatility of these species. The impact was similarly negligible for the unreactive SVOC case discussed in Section 5.2. The changes were larger for the Grieshop (~10%), Robinson (~15%), and Ahamdov (~6%) chemical mechanisms due to their more rapid SVOC chemistry and more rapid decrease in the volatility of the SVOCs, but still did not significantly affect the results for OA. Similarly, the gas-phase impacts of this uncertainty were negligible for the optimized chemistry and unreactive SVOC cases, but could be quite significant (~20% for O₃) for the other mechanisms.

We also tested treating all of the remaining unidentified SVOCs and SVOC₉ ($C^* = 10^6 \mu\text{g m}^{-3}$) instead of SVOC₈ ($C^* = 10^5 \mu\text{g m}^{-3}$). This had little impact (less than 5%) on the OA results for the unreactive, Ahmadov, and optimized chemical mechanisms, but decreased the OA for the

Grieshop and Robinson chemistries by ~25%. The gas-phase impacts on the optimized chemistry were negligible, and led to a 5-10% decrease in O₃ for the other mechanisms.

Finally, we tested a more volatile POA distribution by moving the mass from SVOC3 ($C^* = 1 \mu\text{g m}^{-3}$) to SVOC7 ($C^* = 10^4 \mu\text{g m}^{-3}$). This reduced the OA for the unreactive, Ahmadov, and optimized SVOC chemistry cases by 19%, 7%, and 12%, respectively, but had little impact on the Grieshop and Robinson chemistry cases.

We have added a brief discussion of these sensitivity tests to our revised paper:

P21, L23-26:

Changing the gas-phase concentrations of the unidentified SVOC by $\pm 50\%$ has a small impact ($\sim 3\%$) on these results, but the match between the model and observation could be improved by using a less volatile POA distribution than that given by Grieshop et al. (2009a).

P22, L12-15:

The OA formed using these mechanisms [Grieshop and Robinson] can be reduced by $\sim 25\%$ if we assume the unidentified SVOCs are mainly the more volatile SVOC₉ ($C^ = 10^6 \mu\text{g m}^{-3}$) instead of SVOC₈ ($C^* = 10^5 \mu\text{g m}^{-3}$), but are fairly insensitive to errors in the POA volatility distribution.*

P25, L19-24:

As in Section 5.2, changing the gas-phase concentrations of the unidentified SVOC by $\pm 50\%$ has a small impact ($\sim 3\%$) on these results, as does assuming that the unidentified SVOCs are mainly the more volatile SVOC₉ ($C^ = 10^6 \mu\text{g m}^{-3}$) instead of SVOC₈ ($C^* = 10^5 \mu\text{g m}^{-3}$). However, this result is still sensitive to the POA volatility distribution – for example, moving all the mass in SVOC₃ ($C^* = 1 \mu\text{g m}^{-3}$) to SVOC₇ ($C^* = 10^4 \mu\text{g m}^{-3}$) decreases the modeled $\Delta\text{OA}/\Delta\text{CO}_2$ downwind by 12% for this case.*

On structure, I found the first part (ASP results with no unidentified SVOC chemistry) straight forward and well done, but was completely surprised that OA was ignored here. It is critical to describe how well the model does with OA with no unidentified SVOC chemistry, as this is the context that sets the stage for the next section and justification for including additional SVOC chemistry.

We agree with the reviewer that the structure of our original manuscript was a little confusing here, as the model results for OA with no unidentified SVOC chemistry are not discussed until Section 5.3, when they instead belong in Section 5.2 where the rest of the results for the no unidentified SVOC chemistry runs are discussed.

We have moved the relevant paragraph from Section 5.3 to the end of Section 5.2 and added more quantitative details (P21, L17-31):

Figure 9 shows the modeled OA enhancement ratios ($\Delta OA/\Delta CO_2$, g/g) at 4.5 hours downwind using the parameters listed in Table 2 in addition to the observed average OA enhancement ratio ($2.83 \pm 1.08 \times 10^{-3}$) and the modeled OA enhancement ratio for the case where the chemistry of the unidentified SVOCs is not included (2.27×10^{-3}). When SVOC chemistry was not included, some of the original OA evaporated into the gas phase as the plume diluted, and as there was no chemistry to make these SVOC species less volatile, they stayed in the gas phase leading to a net decrease in $\Delta OA/\Delta CO_2$ with time. Changing the gas-phase concentrations of the unidentified SVOC by $\pm 50\%$ has a small impact ($\sim 3\%$) on these results, but the match between the model and observation could be improved by using a less volatile POA distribution than that given by Grieshop et al. (2009a). However, the modeled decrease without SVOC chemistry is larger (but still within the error bars) than the decrease that was reported by Akagi et al. (2012). In addition, the assumption that the SVOCs do not react is unrealistic – as large multi-functional organic compounds, they should have a relatively fast reaction rate with OH (see Section 5.3 below). Thus in Sections 5.3 through 5.5 below we test different, more realistic implementations for the chemistry of these SVOCs.

Specific comments:

Pg 32435, line 8: Unclear what sectional means here.

In this context, a sectional (or discrete) aerosol size distribution is one in which concentrations are distributed over increments (the “sections” or “size bins”) in radius space (see Section 13.3 of Jacobson, 2005). The sectional representation of aerosol size bins is used in many atmospheric aerosol models (e.g., the MOZAIC model, Zaveri et al., 2008). The basic principles of the approach are discussed in Jacobson (1997, 2007, 2005) as cited in the paper, as well as in Alvarado (2008).

We have revised our discussion in the paper to be clearer on this point (P7, L8-10):

Aerosols are represented in ASP by a single moving-center sectional size distribution, where the aerosol concentrations are distributed over increments in radius space (Jacobson 1997, 2002, 2005).

Pg 32439, line 13: AT this point need to clarify that you will be evaluating the chemistry with parameters in table 5.

We agree, and have added the following sentence to the revised manuscript (P11, L12-15)

Our purpose is less to detail all the possible reactions of the unidentified SVOCs and more to explore how their average chemistry might affect O₃ and OA evolution in smoke plumes. *The specific combinations of parameters for Reactions R3 and R4 that were evaluated in this study are shown in Table 2.*

32446, : Nothing mentions SVOC yet they are in table 4. How are these concentrations obtained, what is the meaning of the different SVOC values and what is the uncertainty? This is critical information. If the concentration of the SVOCs are over estimated, then this could explain a lot.

We agree, and as noted above we have added Table 1 with more information on the SVOC compounds, a further discussion of how the values were obtained, and a discussion of the impacts of uncertainties in these values to the revised paper.

32446, line 27: Units on SD.

Since the aerosol is being represented with a log-normal distribution, the standard deviation here is the geometric standard deviation, and as such is unitless (see Sections 7.1.6 to 7.1.8 of Seinfeld and Pandis, 1998). We have made the following change to the revised paper to show that the lack of units is intentional (P18, L1-4):

The initial smoke aerosol size distribution was assumed to be a log-normal with a geometric mean diameter D_g of 0.10 μm and a standard deviation σ of 1.9 (*unitless*) based on Reid and Hobbs (1998) for flaming combustion of Brazilian cerrado, which structurally is a similar mix of shrubs and grasses as in the Williams fire.

32447, line 9: Section 2.2 says almost nothing about photolysis. I found myself going back and forth between these two sections trying to find more information. There are a lot of additional uncertainties on photolysis rates not mentioned. This includes aerosol bleaching over time, observations that show higher SSA, and the wavelength dependence of SSA. Comments on uncertainties?

We agree with the reviewer that there are many additional uncertainties in the calculated photolysis rates, especially due to the uncertainty in aerosol optical properties as noted by the reviewer. It would be better if future smoke plume studies could have direct observations of photolysis rates made on the aircraft to help reduce these errors, but such data is not available for the Williams fire. However, the range of photolysis rates used in this study is fairly large, covering a factor of two or more from the lowest (slow dilution bottom) to the highest (slow dilution top) photolysis rates throughout the aging period, and so we feel these additional uncertainties in the photolysis rates are likely covered by the range of values considered in this study.

We also agree that Section 2.2 says little about the photolysis rate calculation used for the Williams fire. Our logic was that since many of the values discussed in Section 5.1 for photolysis rates are specific to the Williams fire, it was more appropriate to discuss them in that section. However, we realize how this might be confusing to a reader, and so we have added some of the photolysis discussion from Section 5.1 to Section 2.2 (P8, L30-32 and P9, L1-8):

In the TUV simulations, we assume no clouds and that the initial smoke plume AOD at 330 nm decreases due to dilution assuming a background concentration of ~ 0 , and the aerosol is assumed to have a constant (both with time and wavelength) single scattering

albedo (SSA) of 0.9 based on the review of AERONET biomass burning smoke optical property retrievals by Reid et al. (2005a). We also dilute the initial plume concentrations of the trace gases NO₂ and SO₂ assuming a background concentration of ~0, as these species can also absorb ultraviolet and visible (UV-VIS) light and thus can impact photolysis rates. For the photolysis rate calculations only, O₃ is assumed to be 0 initially and increased after 15 minutes to a constant value based on the observed formation of O₃ within the smoke plume. Section 5.1 has more details on the specific approach and quantitative values used for the Williams Fire.

We have also added the following text to our revised paper to clarify these photolysis issues:

(P19, L8-12): Note that, while our assumption of a constant SSA is questionable as aerosol absorption is likely to change with both smoke age and with wavelength, our use of three dilution rates and three altitudes in the plume results in a wide range of photolysis rates used in this study, which can also account for uncertainties in the aerosol optical properties and other parameters used to calculate the photolysis rates.

(P27, L8-19): Future field experiments, focused on quasi-Lagrangian sampling of biomass burning smoke plumes, may also provide data beyond that available for the Williams Fire that will increase our understanding of the chemistry of these plumes. These include (a) observations of changes in particle size distribution to test model simulations of condensational growth, coagulation, and new particle formation; (b) observations of a larger suite of NO_y species, such as HNO_{3(g)}, peroxy nitrates, and alkyl nitrates, for use in studying and constraining the transformations of reactive nitrogen; (c) direct measurements of photolysis rates within the smoke plumes; (d) measurements of organic aerosol volatility, viscosity and mixing state with black carbon and inorganic aerosols; and (e) more detailed measurements of the currently unidentified organic species present in the smoke plumes.

32448, line 9: I don't understand the value of 1.1e-3, this doesn't sound like its enhanced.

This was a typo, the NO₂ photolysis rate above the plume should be $1.1 \times 10^{-2} \text{ s}^{-1}$, versus a clear-sky rate of $9 \times 10^{-3} \text{ s}^{-1}$. This has been fixed in the revised paper (P19, L5).

Section 5.2: This section does a good job of describing the results with no additional SVOC chemistry and it seems for gas phase, things are in pretty good shape. You need to summarize this section before moving on. But I was quite confused when section 5.2 said nothing about OA. It seems if the authors want to argue for the importance of unidentified SVOCs, now is the time to make your case. At minimum, you must show the model performance for OA/CO₂ for the "no additional chemistry" case and summarize the results of these model runs in section 5.2 before moving on.

We agree, and as noted above we have moved the relevant paragraph from Section 5.3 to the end of Section 5.2 and added more quantitative details (P21, L17-30):

Figure 9 shows the modeled OA enhancement ratios ($\Delta OA/\Delta CO_2$, g/g) at 4.5 hours downwind using the parameters listed in Table 2 in addition to the observed average OA enhancement ratio ($2.83 \pm 1.08 \times 10^{-3}$) and the modeled OA enhancement ratio for the case where the chemistry of the unidentified SVOCs is not included (2.3×10^{-3}). When SVOC chemistry was not included, some of the original OA evaporated into the gas phase as the plume diluted, and as there was no chemistry to make these SVOC species less volatile, they stayed in the gas phase leading to a net decrease in $\Delta OA/\Delta CO_2$ with time. However, the modeled decrease without SVOC chemistry is larger (but still within the error bars) than the decrease that was reported by Akagi et al. (2012). In addition, the assumption that the SVOCs do not react is unrealistic – as large multi-functional organic compounds, they should have a relatively fast reaction rate with OH (see Section 5.3 below).

32451: Again context needed. The best model fit for OA/CO2 seems to be with no additional chemistry! You need to discuss this and clearly explain why the additional chemistry is justified.

As noted above, our results have changed slightly due to our correction of the initial SVOC concentrations, so that now the best fit is for the optimized chemistry case. However, we agree with the reviewer that we need to be clearer in the text on our motivation for using this chemistry, as the OA results for the unreactive SVOCs and using the Ahmadov et al. (2012) chemical mechanisms are both within the uncertainty in the OA observation.

To do this, we have moved the following sentence to Section 5.2 where the unreactive chemistry is discussed (P21, L26-31):

However, the modeled decrease without SVOC chemistry is larger (but still within the error bars) than the decrease that was reported by Akagi et al. (2012). In addition, the assumption that the SVOCs do not react is unrealistic – as large multi-functional organic compounds, they should have a relatively fast reaction rate with OH (see Section 5.3 below). Thus in Sections 5.3 through 5.5 below we test different, more realistic implementations for the chemistry of these SVOCs.

And note the language discussing the gas-phase errors in the Half-fragmentation case (P24, L6-10):

For example, Figure 11 shows that using the “Half Fragmentation” scheme reduced the ASP v2.1 estimates of the enhancement ratios of O_3 and PAN downwind by 24% and 23%, respectively (for the best estimate dilution and photolysis case, the black line in Figure 5), while Figure 12 shows that it increased the ASP v2.1 estimates of C_2H_4 and NO_x downwind by 33% and 151%, respectively.

32455, line 11: Unclear what is “average”.

Here “average” referred to the model runs with the best-fit dilution combined with the middle of the plume photolysis rates, plotted as a solid black line in Figure 5, as stated in Section 5.2

(P32449, L1-2 of the original paper, and P19, L29-30 of the revised version). However, we realize this terminology is confusing and imprecise. In the revised version, we instead refer to this case as the “best estimate dilution and photolysis” case. This is changed in several places in the revised paper.

Table 4: I assume these are ug C per m3. Key omission of information on SVOC1, SVOC2, etc.

These values are in $\mu\text{g m}^{-3}$ like the other values in the table, not $\mu\text{g C m}^{-3}$. As noted above, we agree with the reviewer that we had not adequately defined the meanings of SVOC₁, SVOC₂, etc. in our original paper, and have added a new Table 1 to our revised paper with this information, including the assumed molecular weights of these species. Table 4 is now Table S4 in the Supplemental Material, and contains the revised values noted above.

Figure 1: I don't understand why you use O3 – NO instead of the more conventional O3+NO2 for evaluation. It seems there is a mistake in the caption in the equation for delta O3-NO. The fonts in this figure are very small and should either be increased or omitted.

We use O₃ – NO for the evaluation as this metric has been used previously to assess the performance of the SAPRC-99 (Carter et al., 2005), SAPRC-07 (Carter, 2010), and CB05 (Yarwood et al., 2005) when compared to the EPA chamber data. By using the same metric as these other mechanism evaluations, we make it easier to compare the performance of the ASP v2.1 mechanism to these other approaches.

As noted above, we have removed Figure 1b, which should make the axes and fonts of Figure 1a (now Figure 1) easier to read. We have also fixed the typo in the caption for the definition of $\Delta([\text{O}_3] - [\text{NO}])$, so that it now reads:

Figure 1. ASP calculated hourly values of $\Delta([\text{O}_3] - [\text{NO}]) \equiv ([\text{O}_3]_{\text{final}} - [\text{NO}]_{\text{final}}) - ([\text{O}_3]_{\text{initial}} - [\text{NO}]_{\text{initial}})$ versus the values measured in the EPA chamber of Carter et al. (2005) for 30 “full surrogate” experiments. Note that all time points for the 30 chamber experiments are plotted, not just the final values.

Figure 3: In my print version of this figure, the dashed lines for above plume photolysis have disappeared.

As CO is relatively insensitive to the photolysis rates, we only intended to plot the solid lines shown in Figure 3. However, the legend of the figure was incorrect. This has been corrected in the revised paper, and we apologize for the oversight.

Figure 9: Why is the scale in % when everything else in the paper is g/g? Very confusing.

We agree, and have changed the scale in Figure 9 to be in g/g. However, note that most of the gas-phase results are presented in mol/mol, not g/g.

Anonymous Referee #2

The paper presents an updated version of the atmospheric chemistry box model –Aerosol Simulation Program (ASP) and its application to a young biomass burning (BB) plume. Simulation of NO_x, PAN, O₃, organic aerosol (OA) and other chemical species, and their comparison with the observations are presented. So far atmospheric chemistry models have been struggling to accurately reproduce the ambient OA concentrations. One of the objectives of this modeling study is to improve our understanding of the secondary OA (SOA) formation and evolution within BB plumes. The state of the art volatility basis set approach has been implemented in the ASP model to simulate SOA concentrations. Different variations of the SOA parameterization are tested in this study. Given the scientific importance of understanding the BB impact on air quality and climate, I think this modeling study deserves a publication. However, the authors need to do some reworking before the paper can be suitable for ACP.

My major comment on the study is the treatment of the SVOC chemistry in the ASP model. To my knowledge, majority of the atmospheric models treat the SOA chemistry independently from the gas chemistry [...]

This is indeed the case – most current models assume the SOA and gas chemistry are independent, either by assuming the SVOC precursors of SOA have a negligible impact on the gas-phase chemistry or by adopting the “do no harm” approach of including OH as both a reactant and a product, as discussed on P32454 L5-11 of our original paper. One of our major arguments in this paper is that in the concentrated environment of a biomass burning plume, where much of the NMOC and SVOC mass is present in unidentified compounds, this assumption of the independence of the SOA and gas chemistry is unrealistic, and thus the impact of the chemistry of the unidentified SVOCs on the gas-phase chemistry should be considered.

[...] Here, the authors introduce some chemical reactions for the SVOCs (p. 32438). These reactions are intended to improve the gas phase chemistry simulations along with the SOA simulations. First of all, the authors need to make clear, what laboratory studies are these reactions (e.g. R4) based on? The SVOCs can comprise myriad of different type of molecules, and without knowing their chemical structure how one can treat their reaction products more “explicitly”? For instance, what VOCs are made by the reaction R4?

The Reactions R3 and R4 aren't based on specific laboratory studies, as they are not supposed to represent the “true” chemistry of a specific organic compound, but rather are supposed to be a generic framework that can be used to explain the average, “lumped” reactivity of the likely thousands of compounds (with different oxidation states, volatilities, functional groups, etc.) included in our volatility distribution of the unidentified SVOCs. However, since we do not know the identities of these compounds and their relative concentrations, we still would not be able to explicitly calculate their collective impact on the smoke plume chemistry correctly even if we knew the oxidation chemistry of these compounds exactly (which of course we do not).

Instead, we are simply using R3 and R4 to capture the average, or “lumped”, chemistry of these species, as noted above. This is similar to how mechanisms like RACM2, SAPRC-07, and CB05

deal with different functional classes like alkanes, alkenes, aldehydes, etc., and how the VBS scheme deals with the thousands of compounds involved in OA chemistry. The form of R4 is based on the VBS scheme with fragmentation (which captures the ability of the unknown compounds to form OA) and the idea of the “mechanistic reactivity” of a generic organic species or mixture (which captures the ability of the compounds to form O₃ and recycle HO_x and NO_x radicals.)

This average chemistry is a function not only of the reaction mechanisms of the individual compounds, but also of their relative proportion in the smoke. Our hope is that while identifying all of these compounds in the smoke plumes may prove extremely challenging (although progress is being made, see Stockwell et al., 2015), the method shown here to constrain the average chemistry of these unknown compounds will allow us to determine how the overall chemistry of these smoke mixtures changes with fuel type, combustion conditions, and other environmental parameters.

We have edited our revised paper to clarify this (P10, L18-21):

Thus in ASP v2.1, the *average, lumped* chemistry of the SVOCs is instead parameterized in a more realistic manner for a generic organic species, following the idea of “mechanistic reactivity” (e.g., Carter, 1994; Bowman and Seinfeld, 1994a,b; Seinfeld and Pandis, 1998).

And again at P11, L10-12

Also note that these Reactions R3 and R4 represent the average chemistry of the unknown species collectively, and may not apply to any individual species in that mixture.

The chemical mechanism for the SVOCs and the parameters optimized here are for the Williams fire. Will the same model work for simulations of gaseous and aerosol species in another BB plume?

The answer is that we do not know how representative the chemistry of the Williams fire is of other biomass burning plumes, or even of other plumes from the burning of California chaparral in different conditions (meteorology, fuel moisture, time of the start of the burn, etc.) than those of the Williams fire. As this is our first application of our new approach to the lumped chemistry of the unidentified VOCs in the smoke plume, we cannot be certain how representative it will be of the chemistry of plumes from fires in other ecosystems, different burning conditions, etc. In fact, given the variability of the secondary production of O₃ (see P32430, L26-28 and P32431 of our original paper) and OA (P32432, L17-29) in smoke plumes, it is unlikely that a single set of parameters for Reaction 3 and 4 will successfully simulate all of these cases. Our hope is that this method, if applied to more observations of the chemical evolution of biomass burning smoke plumes, will help to determine how the observed chemistry of the unidentified compounds (and the resulting O₃ and OA formed) depends on fuel type, combustion efficiency, and other parameters, thereby allowing this process to be parameterized in regional and global scale models, as discussed in the conclusions section of our original paper.

We have clarified this issue by making the following changes to our revised paper (Conclusions Section, P26, L28-31):

Furthermore, these specific, quantitative results only apply to the Williams fire analyzed in this paper. Further analysis of other smoke plume observations is needed to determine how these parameters vary between individual smoke plumes.

SVOCs are briefly defined in P. 32429. I think it needs to be made clear whether intermediate VOCs (IVOCs), which are important SOA precursors are included here as a part of SVOCs. Additional literature needs to be discussed regarding this point [...]

As noted on P32437, L13-16 of our original paper, for simplicity we are using the generic acronym “SVOC” to refer to any unidentified compound in the smoke plume with a saturation mass concentration at 300 K (C^*) between 10^{-2} and $10^6 \mu\text{g m}^{-3}$. Some other papers (e.g., Dzepina et al., 2009) use the term SVOC to refer to species with C^* between 10^{-2} and $10^3 \mu\text{g m}^{-3}$ and IVOC to refer to species with C^* between 10^4 and $10^6 \mu\text{g m}^{-3}$. We feel it is simpler to use a single acronym for all of these species.

We have clarified this nomenclature in the revised paper (P9, L13-22):

We use 9 surrogates or “bins” for semi-volatile, intermediate volatility, low volatility, and extremely low volatility organic compounds (hereafter collectively referred to as “SVOCs” for simplicity) as in Dzepina et al., 2009, rather than only 4 as in Ahmadov et al. (2012). The saturation mass concentration at 300 K (C^ , see Robinson et al., 2007) of each SVOC bin differs by a factor of 10, and covers the range from 0.01 to $1.0 \times 10^6 \mu\text{g/m}^3$. Note that “SVOC” as defined in this paper includes both semivolatile organic compounds (C^* between 10^{-2} and $10^3 \mu\text{g m}^{-3}$) and intermediate volatility organic compounds (species with C^* between 10^4 and $10^6 \mu\text{g m}^{-3}$) as defined in Dzepina et al. (2009), but we refer to both of these species classes collectively as “SVOCs” rather than as “S/IVOCs” as in Dzepina et al. (2009) for simplicity.*

[...] If IVOCs were part of SVOCs in the model, then how accurate would be to assume the same chemical reactions (e.g. fragmentation rate) for the chemical compounds with very different volatilities and oxidation degrees?

We agree with the reviewer - we do not expect the exact same chemical reactions will apply to the likely thousands of compounds (with different oxidation states, volatilities, functional groups, etc.) included in our volatility distribution of the unidentified SVOCs. However, as noted above, we do not know the identities of these compounds and their relative concentrations, so instead, we are simply trying to capture the average, or “lumped”, chemistry of these species. Our hope is that while identifying all of these compounds in the smoke plumes may prove extremely challenging (although progress is being made, see Stockwell et al., 2015), the method shown here to constrain the average chemistry of these unknown compounds will allow us to determine how the overall chemistry of these smoke mixtures changes with fuel type, combustion conditions, and other environmental parameters.

We have edited our revised paper to clarify this (P10, L18-21):

Thus in ASP v2.1, the *average, lumped* chemistry of the SVOCs is instead parameterized in a more realistic manner for a generic organic species, following the idea of “mechanistic reactivity” (e.g., Carter, 1994; Bowman and Seinfeld, 1994a,b; Seinfeld and Pandis, 1998).

And again at P11, L10-12

Also note that these Reactions R3 and R4 represent the average chemistry of the unknown species collectively, and may not apply to any individual species in that mixture.

You used the estimates by Grieshop et al. for initial SVOC concentrations (Table 4). Then you show that the ASP model overestimates the SOA concentrations, especially using the Grieshop et al. parameterization. In order the model to match the observations of OA strong fragmentation pathways for SVOC oxidations are assumed here. The SVOC species oxidize and contribute to the SOA increase downwind. Therefore, a question arises; maybe the initial SVOC concentrations for the BB plume are overestimated in the model? I agree that introducing fragmentation in the SOA model makes sense, but as the authors noted the fragmentation used here may be unrealistically too high.

We thank the reviewer for bringing this potential source of error to our attention. As discussed in Pages 1-7 of this response, the initial SVOC concentrations were indeed overestimated in the model runs presented in our original paper. Using the more realistic concentrations of the SVOCs described at the beginning of this response and in Table 1 of our revised paper and Tables S3 and S4 of the Supplemental Material, our quantitative results for the OA formation change. The Grieshop et al. (2009a,b) and Robinson et al. (2007) still overestimate the OA downwind, but not as strongly as previously. The Ahmadov et al. (2012) chemistry is now within the error of the OA observation downwind, but a fragmentation probability of 50% is also consistent with the observed OA downwind, as well as with the observed secondary formation of smaller VOCs like acetic acid. For more details please see our discussion in Pages 1-7 of this response and in response to similar comments by Reviewer #1 above.

You used carbon monoxide (CO) to determine the best-fit model parameters for the dilution. This implies that CO was assumed to be completely a passive tracer. What about the chemical production and loss of CO within the fire plume? How much uncertainty does this approach introduce in determining the dilution rates, consequently in simulating other gaseous or aerosol species?

The reviewer is correct that using the observed CO decay to determine the best-fit dilution rate neglects the chemical loss (via reaction of OH) and production (via many organic oxidation reactions) of CO within the plume. We can quantify the size of this error on our results for the “best estimate of dilution and photolysis” case (i.e., the solid black line in Figure 5) by comparing the ratio of CO and a passive tracer in the model initially and 4.5 hours downwind. Our model shows that relative to a passive tracer, CO increases in the plume by 3.5%. While this change in CO is not zero, it gives a much smaller uncertainty in the best-fit dilution rate than is

implied by our “slow” and “fast” dilution cases, or by the spread in the CO observations seen in Figure 3, so the net chemical production of CO in the plume is not the major uncertainty in determining the dilution rates or the observations of other gas and aerosol species.

We have added a brief discussion of this issue to our revised paper (P16, L11-17):

The observed changes in CO mixing ratio were used to determine the best-fit model initial dilution time scale ($\tau_{mix,o} = 106.9$ s) as well as upper and lower limits of the time scale ($\tau_{mix,o}(0) = 15.0$ s and 212.2 s, respectively), as shown in Figure 3. *Note that this dilution fitting procedure neglects the impact of the chemical production and loss of CO on the observed concentrations, but modeling results with an inert tracer suggest that this error is < 4%, much smaller than the dilution uncertainty represented by our upper and lower limit estimates.*

Figure 5: To calculate the enhancement ratios for O3 CO, while for PAN CO2 species are used. Why not to use the same species (e.g. CO) across the paper for consistency?

We agree that using the same species in the denominator for all enhancement ratios could be more consistent if our paper is considered in isolation. However, we chose to have our enhancement ratios match those used in Table 2 of Akagi et al. (2012) that first discussed the Williams fire observations so that people reading both papers together would find it easy to compare the observations and the model results. Akagi et al. (2012) note that enhancement ratios are most accurate when both species are measured simultaneously by the same instrument or, failing that, through the same inlet, which guided their choice of which species to use in the denominator.

We still think this is the most consistent approach to use for the Williams fire, and so have not changed this approach in the revised paper. However, we have added a line explaining our choice to the revised paper (P19, L21-24):

The choice of whether to use CO or CO₂ in the denominator of the EnR was made on a species-by-species basis to match the choices made in Table 2 of Akagi et al. (2012), which were in turn chosen to minimize the impact of measurement and sampling errors on the EnRs.

We also note that while the Enhancement ratio (EnR) of PAN in Figures 5, 11, and 13 was $\Delta\text{PAN}/\Delta\text{CO}_2$ as in Akagi et al. (2012), in the text we discussed results in terms of $\Delta\text{PAN}/\Delta\text{CO}$. This has been corrected in the text (see P20, L8 and P25, L30).

Additional Changes and Edits:

P2, L1: added “intermediate volatility” to description of SVOCs in the abstract.

P2, L6: Changed “chemistry” to “average chemistry”

P2, L30: Removed phrase “after less than an hour of aging”

P3, L32: Changed “but” to “while”

P10, L13-16 and P38, L17-20: Added a reference to Shrivastava et al. (2013) in discussing the fragmentation of SVOCs.

P12, L18-19: Added definition of off-gassing “(*i.e.*, *re-emission of HCHO and other species from the walls of the reaction chamber*)”

P13, L14: Added units to ROG/NO_x ratio estimates.

P15, L19: Deleted extra word “in”

P19, L27: Removed word “dramatic” from “dramatic underestimate”, and added percentage of underestimate (50%).

P20, L4: Added word “results”

P20, L11-13: Added phrases “after emission” and “4 to 4.5 hours downwind.”

P21, L9: Added HONO detection limit of 10 ppbv.

P23, L18: “determine the variability” changed to “control the outcome”

P27, L4-5: Changed “environmental parameters” to “combustion and environmental parameters”

P27, L18-19: Added “including acetaldehyde, an important PAN precursor.”

P27, L21-28: Added to acknowledgements.

Additional References

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845-865, doi:10.5194/acp-15-845-2015, 2015.

Zaveri, R. A., R. C. Easter, J. D. Fast, *and* L. K. Peters (2008), Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), *J. Geophys. Res.*, 113, *D13204*,
doi:[10.1029/2007JD008782](https://doi.org/10.1029/2007JD008782).